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NITROGEN TRICHLORIDE AS A CHLORINATING AGENT: THE ACTION OF NITROGEN TRICHLORIDE ON ETHYL BROMIDE

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY GEORGE HOPKINS COLEMAN

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In Charge of Thesis

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Recommendation concurred in*

Committee
on
Final Examination*

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NITROGEN TRICHLORIDE AS A CHLORINATING AGENT:
THE ACTION OF NITROGEN TRICHLORIDE ON ETHYL BROMIDE.

This investigation was undertaken in the hope that it might have a bearing on the general question of the positive and negative character of atoms in combination. The problem stated a little more fully is this: Do atoms charged positively or negatively retain their characteristics when in combination? Do the electrical charges on them persist in compounds, or are they formed only when the molecule is divided as in ionization?

The results obtained were not just what had been expected; and a review of the whole field relating to the general problem will not be attempted. A summary, only, of the characteristic action of those chlorinating agents, in which the chlorine is usually considered positive, will be given.

THEORETICAL

I. Chlorine

The idea that elementary molecules such as Cl_2, Br_2, H_2, etc., may consist of a positive and negative atom, was suggested by W.A.Noyes.(1) According to this conception, molecular chlorine may be regarded as consisting partially of positive chlorine. Some typical reactions follow. The first two are the usual reactions of chlorination.

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(1) J. Amer. chem. Soc., 23, 460, (1901).

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(a) (1)

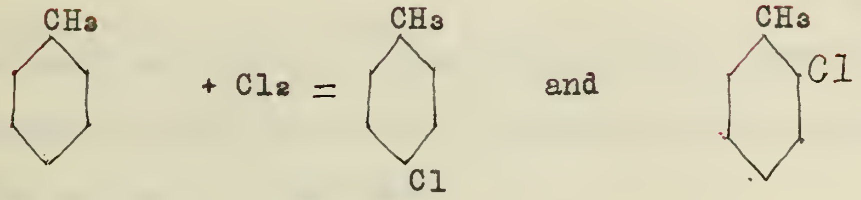
$$CH_4 + Cl_2 = CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 = CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 = CCl_4 + HCl$$

(b) (2)



(c) The work of Lexcoeur (3) on the action of chlorine on ethyl bromide is of interest in this connection. Five products of this reaction were found.

(1) $CH_3\ CHBrCl$ B.P. 84.5°C.

(2) CH_2BrCH_2Cl B.P. 106° C.

(3) $C_2H_3Cl_2Br$ B.P. 137° C. and two isomers of this compound boiling at 151° and 158° - 162° respectively.

II. Hypochlorous acid and calcium hypochlorite.

(a) $2CH_3COCH_3 + 3CaO_2Cl_2 = 2CH_3COCCl_3 + 3\ Ca(OH)_2$ (4)

$2CH_3COCCl_3 + Ca(OH)_2 = Ca(CH_3CO_2)_2 + 2CHCl_3.$

(b) The work of G. Bender (5) is typical of that done by several investigators.

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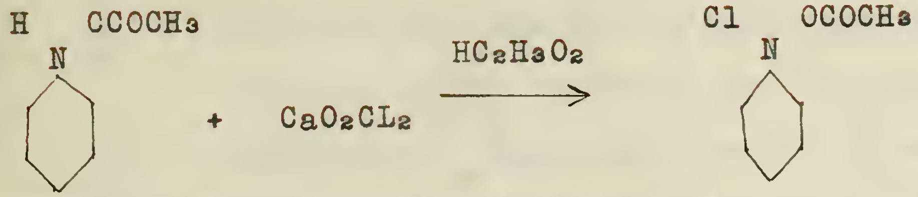
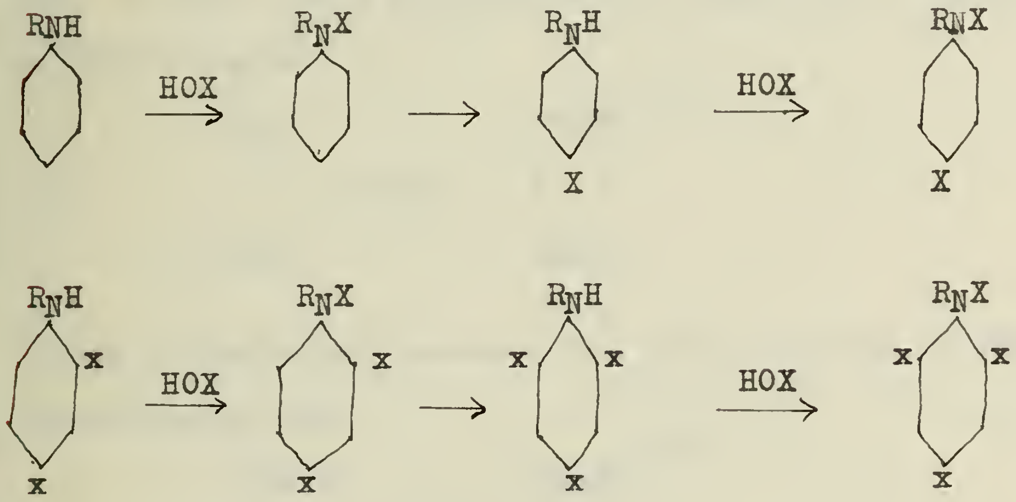
(1) Berthelot, Ann. chim. phys., 3e, <u>52</u>, 97 (1858); Damoiseau, Compt. rend., 83, 60.
(2) Seelig, Ann. chem., <u>237</u>, 152 (1887).
(3) Bl., <u>29</u>, 483 (1878).
(4) Orndorff and Jessel, Am. chem. J., 10, 363 (1888).
(5) Ber., 19, 2272 (1886).

(c)



This substituted nitrogen chloride when heated to 172°C. rearranged to parachloroacetanilide, the melting point of which is 172°.

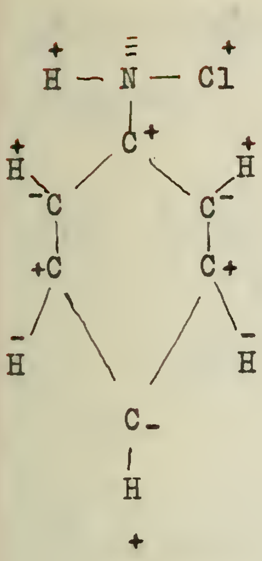
(d) Chattaway and Orton,(1) in a study of the characteristic rearrangements of the substituted nitrogen halides, prepared the following series of compounds.



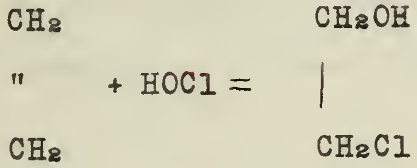
The last compound does not undergo farther rearrangement. In these compounds R may be formyl, acetyl, or benzoyl. The x is either bromine or chlorine. The positions taken by the halogen and the fact that the last does not rearrange is explained by H.S.Fry,(2) according to the structure given below. The positive

(1) Ber., 32, 3572 (1899).
(2) J. Amer. Chem. Soc., 34, 668 (1912).

chlorine may replace the three hydrogens, ortho and para to the nitrogen, that are positive in character. When these are filled no further rearrangement is possible.

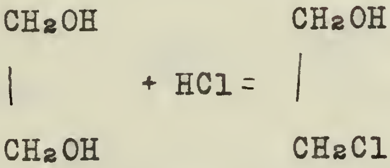


III. A very common reaction is the addition of hypochlorous acid to double bonds.

(a)  (1)

$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + HOCl = \begin{array}{l}CH_2OH\\ | \\ CH_2Cl\end{array}$$

Glycol chlorhydrin, however, can also be prepared from glycol and hydrochloric acid.

 (2)

$$\begin{array}{l}CH_2OH\\ | \\ CH_2OH\end{array} + HCl = \begin{array}{l}CH_2OH\\ | \\ CH_2Cl\end{array}$$

There is evidently, then, a rearrangement of charges in one case or the other.

(b) $CH_3 - CH = CH_2 + HOCl = CH_3CHOHCH_2Cl$ (3)

The chlorine in this addition takes the same position as the

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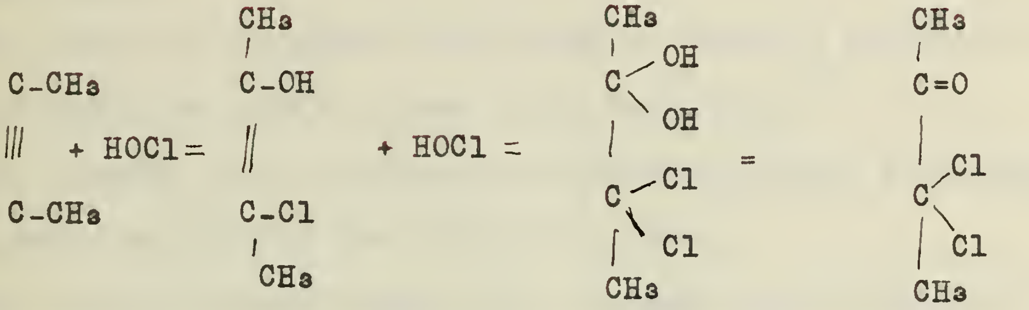
(1) Carius, Ann. Chem., 126, 197 (1863).
(2) Würtz, Ann. Chem. 110, 125 (1859).
(3) Markownikow, Ann. Chem., 153, 228 (1870).

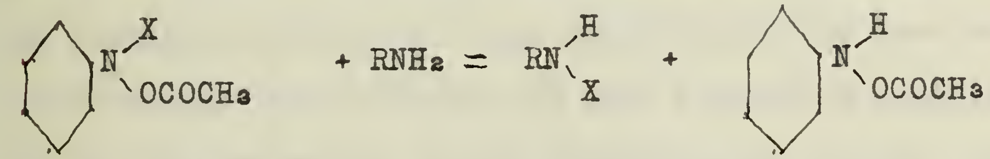
positive hydrogen in the addition of hydrochloric acid to the same compound.

(c) (1)



IV. Beckmann's Rearrangement, J. Stieglitz, (2) presents the idea that on the basis of the electron conception of valence, the initial force causing such rearrangements may reside in the instability of the charges on the radicals held by the nitrogen, and their tendency to go over into their stable forms. Cl^{+} $Cl,^{-}$ $O^{+}H$ $O^{-}H$ etc.

V. Nitrogen chlorides, prepared in the usual way with hypochlorous acid were allowed to act on various amines. Chattaway & Orton. (3)



In the case of anilines the rearrangement to the ring halogen compound may then follow.

VI. Nitrogen Trichloride.

The usual methods for the preparation of nitrogen trichloride

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(1) Faworsky, J. prakt, Chem. 51, 533 (1895).
(2) J. Amer. Chem. Soc., 38, 2046 (1916).
(3) J. Chem. Soc., 79, 461 (1901).

have been the use of hypochlorous acid or free chlorine on ammonium salts.

(a) The action of nitrogen trichloride on various solvents with which it has been used is given by W. Hentschel,(1)

(1) With benzene free nitrogen and hexachorobenzene are formed.

(2) Carbon disulfide yields sulfur chloride.

(3) With carbon tetrachloride only nitrogen and chlorine are formed.

(4) The action with chloroform is a little more involved. Ammonium chloride, hydrochloric acid, chlorine, and a trace of hexachloroethane are formed.

(5) The products with ethyl ether are similar. Ammonium chloride is precipitated, hydrochloric acid and chlorine are liberated, and a liquid boiling between 80° and 150°C. is formed. This liquid was found to contain chlorine, but a complete analysis was not made.

VII. The action of nitrogen trichloride on aniline, methyl aniline, and dimethyl aniline has also been studied by Hentschel.(2) When equimolecular parts of aniline and a solution of nitrogen trichloride in benzene react, trichloroaniline is formed. This compound may also be formed by passing chlorine into a suspension of aniline hydrochloride in benzene. Methyl aniline with nitrogen trichloride similarly gives trichloromethylaniline. On shaking acetanilide with a benzene solution of nitrogen trichloride p-chloroacetanilide is formed. Dimethyl aniline yields a compound having the empirical

(1) Ber. <u>30</u>, 2642 (1897).
(2) Ber., <u>30</u>, 2642 (1897).

formula $C_{24}H_{11}N_2Cl_{19}$. Its structure was not determined.

EXPERIMENTAL.

Various methods for the preparation of nitrogen trichloride were tried. Most of these gave a product containing an excess of chlorine. The method finally used, which gave the purest compound and in very nearly the theoretical amount for the chlorine used was developed by W.A.Noyes, as yet unpublished. A molal sol of ammonium sulfate together with a suitable solvent for nitrogen trichloride, (in this case ethyl bromide itself was used), was surrounded with a freezing mixture , -10° to -20°C, and into this chlorine, at the rate of 0.3 to 0.4 gram per minute, was passed. The delivery tube passed through the aqueous solution into the ethyl bromide at the bottom. The proportions of the materials used were twelve atoms of chlorine to eight mols of ammonium sulfate, the following reaction probably occurring.

$8\ (NH_4)_2\ SO_4\ +\ 6Cl_2 = 2NCl_3\ +\ 8NH_4HSO_4\ +\ 6NH_4Cl$

The solutions were kept in intimate contact by means of a stirrer, operated by a small motor. The stirring was continued during the evolution of the chlorine, and for two hours afterward. The results of several experiments seemed to show that the reaction for the formation of nitrogen trichloride was nearly complete at the end of this time, and that longer stirring was unnecessary. As long as the solution was kept at this low temperature there was no apparent reaction between the nitrogen trichloride and ethyl bromide.

At the end of two and a half to three hours stirring, the

length of time required depending on the amount of chlorine used, the ethyl bromide solution was separated from the aqueous part and dried for a few minutes with calcium chloride. The solution was now a clear yellow, it being slightly opalescent before drying. After filtering through dry asbestos, samples were taken and the remainder of the solution placed in the reaction bulb A of figure 1.

The analysis of the nitrogen trichloride solution was carried out as follows: The nitrogen was determined with concentrated hydrochloric acid, a method which was found by W.A.Noyes to give much better results than the usual sodium sulfite reduction, the reaction being $NCl_3 + 4HCl \quad NH_4Cl + 3Cl_2$. The ammonia was then determined by distillation from alkaline solution. The chlorine and bromine, which were also present, were determined in another sample by Volhard's method, after reduction with sodium sulfite and the addition of exactly enough potassium permanganate to oxidize the excess sulfite. The precipitated silver halides were filtered off and weighed in a gold Gooch crucible, and the chlorine and bromine calculated by the indirect method.

In taking the samples for analysis one hundred cubic centimeter Erlenmeyer flasks were used. The concentrated hydrochloric acid or sodium sulfite was placed in the flask and a little ethyl bromide added, in order that the vapor in the flask should be the same before the sample was added as after. The flasks were weighed to an accuracy of one hundredth of a gram and placed in a freezing mixture. As soon as they were thoroughly cooled, the samples, (2.g. to 5g. of solution), were added. After shaking the flasks gently they were removed, allowed to come nearly to room temper-

cense, soon becoming a white precipitate. The temperature of the solution also rose until it was necessary to cool it to prevent vaporization. After keeping the temperature below twenty-five degrees for two or three hours, there seemed to be no tendency for it to rise above that of the room.

During the course of the reaction the solution turned a darker yellow, but not, however, the reddish color of free bromine in ethyl bromide. The evolution of gas was more rapid during the first twenty-four hours, but continued slowly for four to six days in most cases. When the reaction at room temperature, about twenty-five degrees, was complete, the bulb was placed in a water bath, kept at thirty degrees, for two hours. During this time a small additional amount of gas evolved. The analyses of the several products will be discussed separately.

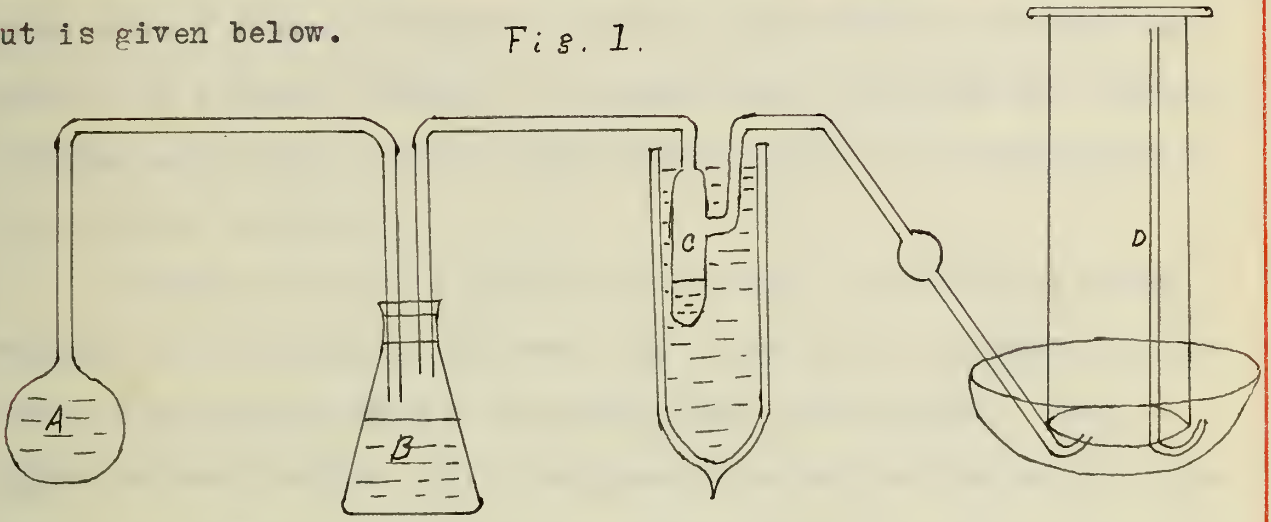
The contents of the reaction flask were filtered through a weighed Gooch crucible into an excess of sodium sulfite solution. The flask and the contents of the crucible were washed several times with ethyl bromide. After thorough shaking the two solutions were separated. The nonaqueous solution was dried with calcium chloride and distilled. As expected, the greater part was ethyl bromide, but there was also found a small amount of a much higher boiling liquid.

The white salt in the crucible was freed as far as possible from the ethyl bromide and dissolved out with water. This solution was evaporated in a weighed dish. This salt on analysis for chlorine and ammonia proved to be pure ammonium chloride. The

ature, carefully wiped and weighed. Except when the samples were added the flasks were covered with small watch glasses.

A diagram of the apparatus in which the reaction was carried out is given below.

Fig. 1.



The bulb A was of such a size in each case that the solution filled it within a few cubic centimeters. The flask B contained an excess of sodium sulfite solution. The U tube C was surrounded with a freezing mixture contained in a Dewar flask. The temperature was not allowed to rise above eight or ten degrees below zero centigrade. The gas passing beyond tube (C) was collected in a graduated cylinder, from which it could again be removed by tube (D).

In carrying out the reaction the ethyl bromide solution was placed in the bulb (A). As soon as possible after removing it from the freezing mixture. This bulb was protected from the light throughout the experiment. For some time, usually from thirty minutes to an hour, there was no apparent change in the solution. The first evidence of reaction was a slight opales-

crucible was dried in a vacuum and weighed. The gain in weight in the one case tried, was only 1.1 mg., and in this, as in the following, a slight blackening of the asbestos on heating indicated only a trace of organic matter. The sulfite solution was made up to a known volume, and aliquot parts analyzed for ammonia chlorine and bromine by the same methods used in the analysis of the original solution.

That part of the gas evolved during the reaction which reached the collecting cylinder, was found to be nitrogen on the basis of molecular weight determinations, as follows: From eighty to one hundred cubic centimeters were transferred to a gas burette and measured at atmospheric pressure. This was allowed to enter a weighed, evacuated bulb of known volume. The bulb was then weighed, air admitted at atmospheric pressure, and the bulb again weighed. Two methods for calculating the molecular weight were thus furnished. The following weights from different experiments were found, 32.3, 31.9, and 29. There seems little doubt, therefore, that the gas was nitrogen, with perhaps a little ethyl chloride vapor. The evidence for this will be given next.

The results of two experiments only, in which different methods of detecting ethyl chloride were used, will be discussed.

After the completion of the reaction the U tube (C) was connected directly to a gas burette and removed from the freezing mixture. When the tube was warmed up to about 15°C. eighty-five cubic centimeters of gas were evolved, which was found to have a molecular weight of seventy-seven. The same method was used here

as in the case of the nitrogen.

In the second, an attempt was made to distill the ethyl chloride and determine its boiling point, but without much success. The liquid in the U tube was heated slowly to 30°C and the distillate of one cubic centimeter collected in the bulb of the apparatus shown in figure 2, which was immersed in a freezing mixture. A thermometer and boiling tube were inserted, the U tube surrounded with a freezing mixture, and the temperature of the bulb slowly raised. Bubbles began to appear at about 10°C, but no definite boiling point seemed to be reached. One-half cubic centimeter was distilled from this U tube into a small test tube. This was immediately attached to a bulb, of known volume and weight, with capillary openings at each end. A small tube attached to the upper opening carried the vapors into a second test tube surrounded with a freezing mixture. The liquid in the first test tube was warmed and as soon as one drop of distillate appeared, the ends of the bulb were sealed. The bulb was now weighed, and then immersed in a freezing mixture, at -10°C, and one of the tips opened. From the weights and the volume of the water entering the bulb, the molecular weight of the gas was found to be eighty-three. Both in this case and in the previous one, a mixture of ethyl chloride and ethyl bromide would give the molecular weight found.

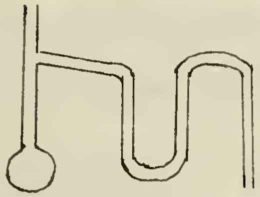


Fig. 2.

While this evidence is not conclusive, it seems very probable that a small amount of ethyl chloride is formed in this reaction.

The sulfite solution in the flask B was made up to a known volume and analyzed for chlorine, bromine, and ammonia in the same way as that described for similar determinations above.

The following tables give the entire analyses of several runs expressed in milligram atoms and milligram mols.

Table 1., (92.g. $C_2H_5BrSol.$)

84.7	mg. mols	NCl_3
242.	" atm.	Cl
50.9	" "	Br
3.16	$\frac{Cl + Br}{N}$	
Residue in bulb.		
6.08	mg. atm.	Cl
4.32	" "	Br
0.7	" mols	NCl_3
34.1	" "	NH_4Cl
Gas evolved.		
37.25	mg. atm.	Cl
17.16	" "	Br
46.8	" "	N
0.13	" mols	NCl_3

Table 2., (287.6g. C_2H_5Br Sol).

276	mg. mols	NCl_3
721.5	" atm	Cl
182	" "	Br
2.92	$\frac{Cl + Br}{N}$	
Residue in bulb.		
276.6	mg. atm.	Cl
34.6	" "	Br
27.08	" mols	NCl_3
65.1	" "	NH_4Cl
Gas evolved.		
145.26	mg. atm.	Cl
21.34	" "	Br
86.4	" "	N
1.08	" mols	NCl_3

Table 3.	Table 4.
280.5 g. C_2H_5Br. Sol.	380g. C_2H_5Br. Sol.
254.5 mg. mols NCl_3	345.0 mg. mols NCl_3
777.0 " atm. Cl	984.0 " atm. Cl
87.0 " " Br	91.4 " " Br
3.39 $\frac{Cl + Br}{N}$	3.105 $\frac{Cl + Br}{N}$
Residue in bulb.	Residue in bulb.
104.88 mg. atm. Cl	368.0 mg. atm. Cl
6.52 " " Br	27.0 " " Br
13.43 " mols NCl_3	68.72" mols. NCl_3
59.2 " " NH_4Cl	72.5 " " NH_4Cl
Gas evolved	Gas evolved
204.9 mg. atm. Cl	147.1 mg. atm. Cl
39.4 " " Br	34.0 " " Br
90.0 " " N	N not collected.
0.77" mols. NCl_3	0.77 mg. mols. NCl_3

Since the amounts of ethyl chloride were undetermined, it is not recorded in these tables.

It was mentioned before, that in each case the reaction bulb was found to contain a small fraction, with a boiling point much above that of ethyl bromide. These high boiling fractions from all the experiments were united and distilled. The total amount of nitrogen trichloride used in the work from which this

liquid was obtained was about 125g., the ethyl bromide used about 1250g. Upon repeated fractionation the fractions given in table 5 were obtained.

Table 5.

Temp.	Vol.	Temp.	Vol.
75 - 79	0.5 c.c.	115 - 120	0.2 c.c.
79 - 80	4.0 c.c.	120 - 125	0.2 c.c.
80 - 84	0.8 c.c.	125 - 130	0.2 c.c.
84 - 88	0.6 c.c.	130 - 135	0.2 c.c.
88 - 92	0.3 c.c.	135 - 140	0.2 c.c.
92 - 96	0.5 c.c.	140 - 145	0.1 c.c.
96 - 101	0.5 c.c.	145 - 150	0.5 c.c.
101 - 103	4.0 c.c.	150 - 152	0.5 c.c.
103 - 106	.4 c.c.	152 - 155	0.6 c.c.
106 - 110	.3 c.c.	155 - 157	4.0 c.c.
110 - 115	.3 c.c.	157 - 161	0.5 c.c.

There was a small residue boiling above 160°C. The three principal fractions were found to contain both chlorine and bromine but no nitrogen. Complete identification has not been carried out.

DISCUSSION OF RESULTS

This work was undertaken with the thought that the reaction might yield triethyl amine and free chlorine and bromine, or perhaps a chlorbromine compound.

$$\overset{\equiv}{N}\overset{+++}{Cl_3} + 3\ \overset{+}{C_2H_5}\overset{-}{Br} \qquad (\overset{+++}{C_2H_5})_3\overset{\equiv}{N} + 3\overset{+}{Cl}\overset{-}{Br}$$

A reaction of this kind would of course be of much interest in relation to the general problem of the positive and negative character of the atoms in compounds. No evidence was found, however, that the reaction took place in this manner. That the nitrogen trichloride did act as a chlorinating agent to a slight extent, is evidenced by the analysis of the three higher boiling fractions of the residue. While this part of the work is not complete, the results obtained seem to show that the products may not be the same as those found by Lescoeur (1) in the action of chlorine on ethyl bromide.

Perhaps one of the most interesting results of the wok was found in the analysis of the ethyl bromide solution before the reaction began. It will be noticed from the tables, that in each case there was quite an appreciable amount of bromine present. From the color of the solution this was not in the free condition. The ratio of chlorine plus bromine to nitrogen, was in each case, very close to three and in solution (2) slightly below that. Whether this may indicate the presence of nitrogen tribromide, a mixed compound, or monochlor or brom amine is a problem that will not be taken up here.

As shown by the tables there is a loss of chlorine, bromine and some nitrogen which is not accounted for by the analyses. At least a part of the loss of chlorine may be attributed to the formation of the organic chlorobromo compounds found in the residue.

(1) Bl., 29, 483 (1878)

The presence of the ammonium chloride suggests that its formation may be due to a reaction between nitrogen trichloride and hydrochloric acid. The possibility of such a reaction in a dry solution has been shown by W.A.Noyes.

CONCLUSION

The products obtained in this investigation of the action of nitrogen trichloride on ethyl bromide were, chlorine, bromine, ammonium chloride, nitrogen, some evidence of ethyl chloride, and small amounts of three organic chlorobromo compounds. No evidence of ethyl amine or its compounds was found.

The existence of a compound of bromine with nitrogen may be indicated by the fact that bromine, not in the free state, was found in the nitrogen trichloride solution.

ACKNOWLEDGEMENT

The writer wishes, at this time, to express his appreciation for the invaluable assistance of Professor W.A.Noyes under whose direction this research was done.

G. H. Coleman.